DDT Residues in Salinas River Sediments

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As the Salinas River meanders across the length of Monterey County, California and finally empties into Monterey Bay, it is a repository for industrial waste water and sewage as well as irrigation return flow. Major urban areas of Soledad, Gonzales, Chualar, and Salinas border the Salinas and discharge sewage either directly into or into ponds in the vicinity of the river. Almost all the agricultural land in Monterey County is located in the Salinas Valley. The economy of the valley centers around crops such as lettuce, strawberries, carrots, artichokes, celery, onions, sugar beets, tomatoes, and asparagus with much of the water used for irrigation of these crops being discharged into the river. During the low summer flow, according to a Department of Water Resources special investigation (8), water in the lower Salinas River is almost entirely due to domestic waste and irrigation return water.

Historically, the chlorinated hydrocarbon, DDT and its derivatives has been used as an insecticide on the wide variety of crops grown in the area as well as for insect control in the urban centers of the valley. The State of California Department of Agriculture recorded that 1,582.00 pounds of DDT was used on 1,008.50 acres in Monterey County during the first quarter of 1970 (6). Since the date for discontinuation of DDT usage, except for on onions, in Monterey County was July 15, 1971, it seems reasonable to assume that a similar amount of DDT was used during the first quarter of 1971. Prior to 1970 accurate tabulations of pesticide use were not made by the Department of Agriculture. However, it can be assumed that the current use levels are considerably below the amounts used in prior years. Therefore, a considerable burden level probably exists in the agricultural soils of the valley. Waste water from the areas where DDT is used carries off a portion of the chlorinated hydrocarbon and deposits it in the Salinas River where it is eventually translocated to the ocean. Since DDT is not water soluble, it is probably primarily carried adsorbed to fine particulate matter in the water which can settle and build up measurable concentrations of DDT residues along certain portions of the river bed.

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In order to gain some indication of the amount of DDT residues in the Salinas River, their areas of concentration, and their rate and mode of translocation, analyses for DDT in sediments taken from selected sites along the river over a period of four weeks were made.

MATERIALS AND METHODS

EXTRACTION PROCEDURE. Approximately 100 grams of the top three inches of river bottom sediment was collected weekly from April 27 to May 17, 1971 in 1 liter glass reagent bottles at each of eight sites along the Salinas River. The sites ranged from the Highway no. 1 river crossing in the north to the Soledad river bridge in the south. See Figure 1. The water was drawn off the

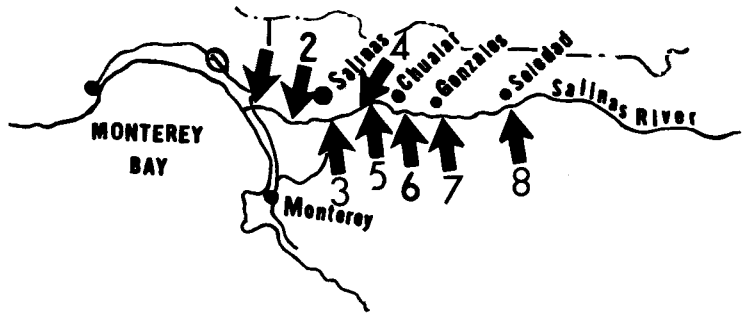

Figure 1. Map of Salinas River Valley with location of collection sites. Site 1 - Highway no. 1 river crossing, Site 2 - Davis river crossing, Site 3 - Spreckles Boulevard river crossing, Site 4 - 1 mile below Spreckles Refinery, Site 5 - $\frac{1}{2}$ mile above Spreckles Refinery, Site 6 - Chualar river crossing, Site 7 - Gonzales river crossing, Site 8 - Soledad Highway no. 101 river crossing.

sample and discarded. In order to extract the pesticides from the sediment, 100 ml of a 20% Acetone - 80% Hexane solution was added. The collecting bottle was then placed on a platform shaker for seventeen hours, after which time 100 ml of distilled water was added in order to raise the hexane layer. Most of the hexane was drawn off and passed through a glass funnel containing Whatman silicon treated 15 cm phase separating paper and collected in a standard taper 500 ml Florence flask. In order to insure quantitative transfer as well as break any emulsion remaining in the collecting bottle, three washes of 50 ml each of a 50% Acetone - 50% Hexane solution were made. The hexane in each case was drawn off and collected in the Florence flask after passing through the phase separating paper.

CLEANUP PROCEDURE. If the hexane extract containing the pesticide residues was highly pigmented, 0.2 grams of Kensco Acid Washed Nuchar Attaclay Mixture was added. After swirling, the Nuchar Attaclay was removed from the solution by making a quantitative transfer using hexane rinses through a glass funnel packed with a small amount of Filtering-grade Pyrex wool. The relatively clear extract was then concentrated to 1.0 ml on a Buchler Flash evaporator. Removal of extraneous co-extractives from the pesticide residue extract was accomplished by using a modification of the Kadoum (3), Law and Goerlitz (5), and Johnson (2) silica gel column cleanup procedure where the microcolumn was packed with 1:25 Nuchar Attaclay - Silica gel adsorbent, Fisher S-662, 60 - 200 mesh.

Approximately 30 minutes before injecting the cleaned extract into the gas-liquid chromatograph, 0.5 ml of metallic mercury was added according to the procedure outlined by Goerlitz and Law (4) in order to remove interference by sulfur containing contaminants. The solution was vortexed for a minimum of five minutes and allowed to stand until the time of injection. If concentration of the extract was required, it was done over a hot water bath by a gentle stream of dry nitrogen.

GAS CHROMATOGRAPHY. A suitable aliquot of the cleaned pesticide residue extract was injected into a Beckman GC4 gas-liquid chromatograph equipped with a helium glow discharge electron capture detector. The pyrex glass column contained a mixed bed of 6% QF-1 and 5% DC-200 on 80/100 mesh Chromabsorb W which was acid washed and DMCS treated. The column temperature was 200°C. The carrier gas, helium, was passed at 60 cu. cm./min.

RESULTS AND DISCUSSION

With the exception of one collection site, Site 2 Davis river crossing, the levels of DDT derivatives along the Salinas River were fairly constant ranging in most cases below the 10 ppb level. See Figure 2. At Davis, however, total DDT derivatives reached well above the 100 ppb level with the concentration of DDE, DDD, and p,p' DDT individually reaching, on several occasions, above 100 ppb. Only on the May 17 collection did the total of all the residues fall below the 200 ppb level.

Casual field observations indicated that the water flow and the bottom sediment at the Davis collecting site were different from other areas under investigation. The sediment was much darker, almost black, instead of the light brown observed at all other points. The bottom sediment also appeared to be made up of finer sediments which could be stirred up with ease. Rather

than a thin layer of silt as observed on the bottom at all other collecting sites, there was a layer of fine sediment approximately 1-2 inches deep. A heavy repugnant odor also seemed to be common only to this area.

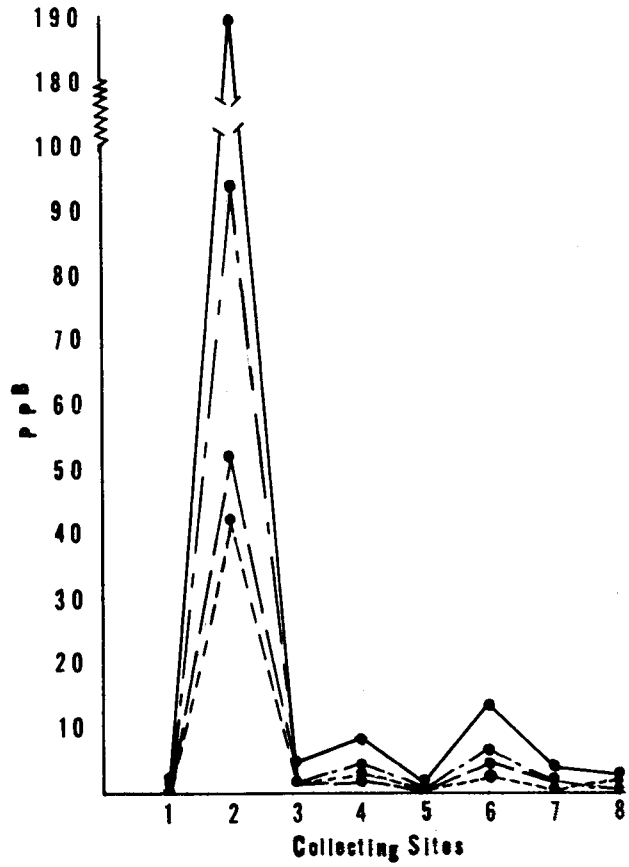

Figure 2. Concentration of DDT derivatives at collecting sites 1-8, see Fig. 1 for location, on May 17, 1971. ——● Total DDT derivatives, —·—·— DDE, ●---●---● DDD, ●—·—·—● p,p' DDT.

In order to quantify the observations made concerning sediment size, all of the dried sediment samples were passed through a series of Tyler wire meshes: 12, 16, 32, 60, 115 mesh/inch, and Pan. By measuring the weight of the sediment held by each screen, the percent of fine sediment, the sediment in the Pan, in each area was determined. The sediment collected at the Davis crossing was usually composed of finer particles than other sites along the river. See Figure 3. It was also found, to the 99% confidence level, that the highest DDT derivative

content of the sediment positively correlated with the finest sediment size. It is probable that the DDT residue concentrations are highest at the Davis site because of the large amount of fine particulate matter being concentrated in the area.

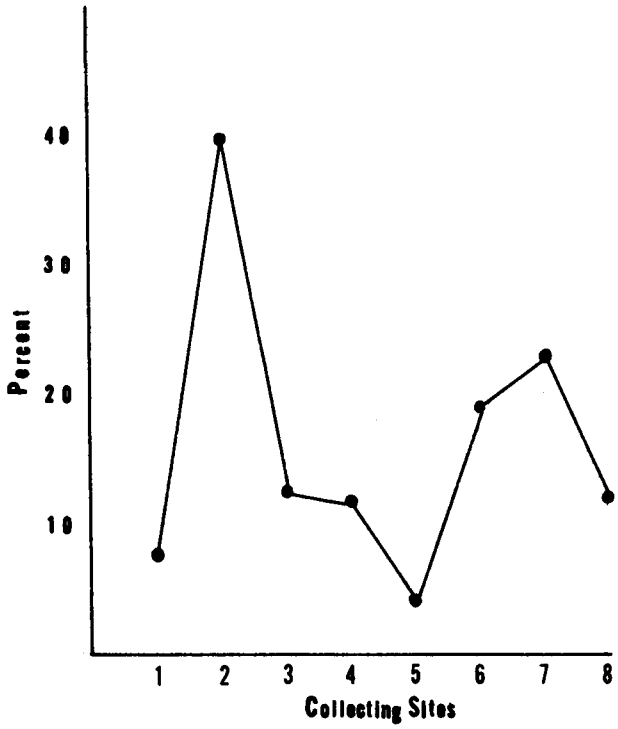

Figure 3. Average percent of Pan size sediment, see text for method of distinguishing size, in samples collected at sites 1-8, see Fig. 1 for location.

Davis is probably a depository for fine sediments because of peculiarities in river topography as well as the fact that the rate of water flow is lower there than at sites located further up stream. See Figure 4B. There is an increase of flow at the Highway no. 1 crossing because a major agricultural drainage system, the Blanco Drain discharges directly into the Salinas River approximately three miles upstream from Site 1. No data could be obtained on the actual flow rate at Site 1, but a reasonable estimate would be 2,000 cu. ft./sec.

The amount of sediment translocated along the river at any particular time appears to be a function of the rate of water flow: the higher the rate, the

greater the sediment content. Water samples were collected in 1 liter glass bottles at Site 6 - Chualar river crossing on three different occasions - May 3, 10, and 17. The samples were left undisturbed for two days. In samples collected on the first two dates, conspicuous sediment precipitated to the bottom of the bottle. By measuring the weight of this precipitate, it was estimated that 1,209.60 kg. of sediment was transported past this site each day. It should be noted that these sampling times corresponded to the period of highest water flow. See Figure 4B.

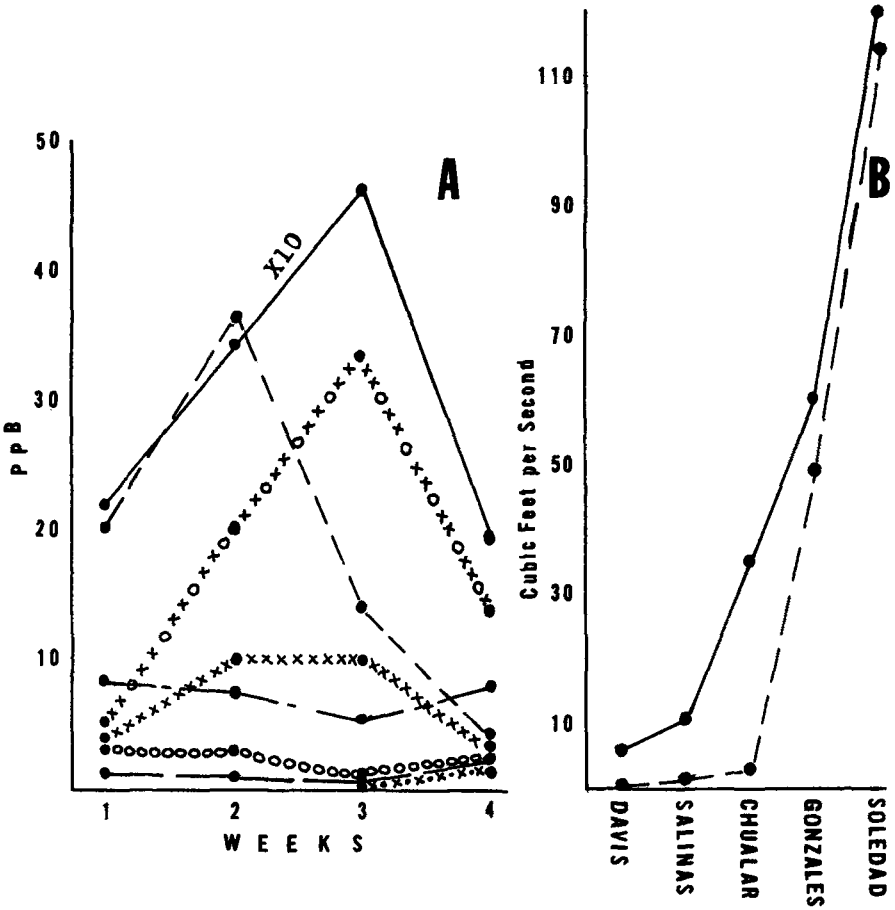

Figure 4. (A) Total DDT derivatives each week at collecting sites 1-8 over the four week period of April 27 to May 17, 1971. Site 1, Site 2, Site 3, Site 4, Site 5, Site 6, Site 7, Site 8.
(B) Water flow rate estimates at selected

sites along the Salinas River based on Department of Water Resources Curves and field measurements.
●——●——● Maximum flow on May 6, 1971
●- - - - -● Flow on May 24, 1971.

The sediment which precipitated from the water samples was also analyzed for DDT content. Total DDT derivatives averaged about 76 ppb on the first two collection dates, about three times the total residues found in bottom sediment samples at the same time. No measurable amount of sediment precipitated from the May 17 water sample, so the entire sample was analyzed for DDT content. The total of all derivatives was found to be 31 ppt which is of the same order of magnitude found in analyses made by the Department of Water Resources near Spreckles in 1966-67 (7). These results suggest the order of magnitude of DDT residues translocated adsorbed to sediments. However, a larger series of water born sediment samples must be analyzed in order to more accurately establish the range of absolute amounts.

Since there is a positive correlation between fine sediment size and DDT derivative concentrations, the amount of pesticide in a given area would be expected to fluctuate with the rate of water flow which would influence the amount of fine sediment carried into or out of an area. In addition, the nature of the fine sediments translocated under conditions of different water flow could influence the concentration of DDT derivatives in these sediments. According to curves used by the Salinas branch of the Department of Water Resources, the maximum water flow was May 6, 1971 (9). See Figure 4B. The second and third weeks of the collection period corresponded to this time of maximum flow. During this period, higher concentrations of Total DDT derivatives were found at Sites 2, 3, 6, and 7. See Figure 4A. These sites were previously seen to be the ones to have bottom sediments composed of the finest particulate matter, Figure 3, and could be termed "depository areas." The remaining sites were areas composed of coarser sediment which would indicate that they were non-depository and would lose sediment during higher flow periods as Figure 4A indicates.

When sites 4 and 5 are viewed together, it is apparent that on the two dates measurements were taken at both sites, the DDT residue levels were higher just below the Spreckles Sugar Beet Refinery than levels in samples taken just above the factory. See Figures 2 and 4A. Seepage from waste water disposal ponds operated by the refinery enters the river slightly above Site 4. Wash water from the beets would carry a large amount of fine soil sediment and pesticides.

According to Figure 3, there is a higher proportion of fine particles in sediment samples taken directly below the factory which could possibly account for the slightly elevated pesticide levels at Site 4.

The main pesticide residue found in sediment at the Highway no. 1 crossing was p,p' DDT. For the most part, there was a tendency for the DDT level to be higher at every site along the river than either of the other two residues measured at the same time and place. In the case of Site 1, the p,p' DDT level was never high, about 1 ppb, when compared with other sites, but it was always about three times as high as the DDE level and four times as high as the DDD concentration. It appears then that the major DDT residue being translocated is p,p' DDT.

SUMMARY

The chlorinated hydrocarbon, p,p' DDT is the most common DDT derivative in bottom sediment samples taken at sites in the Salinas River from the Soledad to the Highway no. 1 river crossing. Its concentration as well as the concentration of total derivatives varies from site to site along the river as well as over time. This is probably due to certain areas acting as natural depositories for water translocated suspended fine particulate matter containing high concentrations of DDT. If the rate of water flow is sufficiently low and if other unspecified natural factors are right, the particles settle and collect at sites along the river yielding a high concentration of DDT residues. Evidence which supports this hypothesis is that the areas with the finest sediment are the areas which also have the highest concentration of DDT derivatives. The portion of the Salinas River south of the Davis river crossing shows the highest concentration of the areas studied.

ACKNOWLEDGEMENTS

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